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Method and device for hydrolytically obtaining a carboxylic acid and alcohol from the corresponding carboxylic ester

The present invention relates to a process, and also to an
5   apparatus, for improved hydrolytic cleavage of carboxylic
esters to the corresponding carboxylic acid and alcohol, in
which at least a portion of the water required for hydrolysis
is replaced by a recycled mixture comprising carboxylic acid
and water which results from the hydrolysis of carboxylic ester
10   already converted in the process.

The inverse of esterification is the hydrolysis of the
carboxylic ester to carboxylic acid and alcohol. Like the
esterification itself, the acid-catalyzed hydrolysis is an
15   equilibrium reaction. Carboxylic esters are used in the
chemical industry, for example, as solvents or plasticizers, or
are obtained in various reactions as by-products or main
products. For example, methyl acetate is a typical by-product
in the preparation of polyvinyl alcohol. Mixtures comprising
20   methyl acetate which are obtained in the preparation of
polyvinyl alcohol, in addition to a small amount of low-boiling
substances, for example acetaldehyde, comprise an azeotropic
mixture of methyl acetate and methanol. Mixtures of the
composition described can be economically utilized only with
25   difficulty, if at all, without further purification or cleavage
(hydrolysis) of the carboxylic esters to the reactants.

The hydrolysis of carboxylic esters can be carried out
batchwise or continuously. Suitable for this purpose is a
30   reactor in combination with a conventional distillation or a
reactive distillation column. The use of a reactor in
combination with a distillation column for the hydrolysis of
methyl acetate is described, for example, in the patent US
4,352,940. The process described there for hydrolyzing methyl
35   acetate is disadvantageous, among other reasons, because the
yields are small and a plurality of distillation stages is
necessary. In addition, corrosion occurs as a result of the use
of sulfuric acid or hydrochloric acid as homogeneous catalysts.

The patent specification US 5,113,015 describes a process for hydrolyzing methyl acetate, in which methyl acetate and water are contacted with a catalyst packing in a distillation column,

5 which hydrolyzes methyl acetate to acetic acid and methanol and at the same time at least partially separates the reaction mixture in the separating column.

The patent specification US 5,770,770 likewise discloses a

10 process for hydrolyzing a methyl acetate mixture in a reactive distillation column, in which the hydrolysis of a methyl acetate stream containing at least 50% by weight of methyl acetate takes place in a reaction zone having an ion exchanger packing. The methyl acetate mixture and water are conducted in

15 countercurrent over the ion exchanger packing. Unconverted methyl acetate and water are recycled into the reaction zone. The hydrolysis products are removed from the bottom fraction. The impurities are recycled back into the reaction zone.

20 The teachings of the patents US 5,113,015 and US 5,770,770 is the use of strongly acidic ion exchangers as catalysts for the hydrolysis of carboxylic esters. The patent US 5,770,770 further describes the use of the ion exchanger material preferably in the form of Raschig rings, whereas, in US

25 5,113,015, the catalyst material is preferably used in the form of mats. The catalyst packing material used may be pliable, open-meshed substances, for example wire mesh, rigid, cellular monoliths of steel, polymers or ceramic material, and also corrugated metal, plastics or ceramic plates.

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The last few processes described which use only a single reactive distillation column have the disadvantage that methyl acetate is only partly hydrolyzed. The reactant stream makes necessary the use of at least one additional purification

35 stage. It is also disadvantageous that metal ions from the methyl acetate feed deactivate the catalyst in the reactive distillation column, which leads to short on-stream times of such continuous plants.

The European laid-open specification EP 1 220 825 A2 describes a process in which the feed stream comprising the carboxylic ester is fed into a prereactor in which the carboxylic ester is contacted with a first catalyst in the presence of water, which partly hydrolyzes the carboxylic ester to the hydrolysis products. The reaction mixture from the prereactor is passed into a reactive distillation column and is contacted with a second hydrolysis catalyst for the purpose of at least partial conversion of the remaining carboxylic ester to the corresponding carboxylic acid and alcohol.

The process described in EP 1 220 825 has the advantage that a higher conversion rate can be attained than in the aforementioned processes. In addition, the use of a prereactor improves the on-stream time of the reactive distillation column, since catalyst poisons, for example metal ions, remain principally in the prereactor. The selection of the particle size of the catalyst material used in the prereactor is less restricted than for the structured catalyst packings used advantageously in the reactive distillation column.

Even when there is initial increased recycling of methyl acetate-rich top stream of the reactive distillation column to the prereactor, the capacity using an existing structure is limited as a consequence of the fixed geometry of the reaction part of the reactive distillation column.

The process described in EP 1 220 825 also has the disadvantage that, when the feed stream of carboxylic ester comprises the corresponding alcohol, the chemical equilibrium of the acid-catalyzed hydrolysis is shifted unfavourably for the products in the reaction part of the reactive distillation column.

The present invention has the object of providing an improved process and also an apparatus for acid-catalyzed hydrolysis of carboxylic esters by means of a reactive distillation column. It is a further aim of this invention to attain high conversion

rates of carboxylic esters to alcohol and carboxylic acid with simultaneous use of mixtures of the carboxylic ester with the corresponding alcohol in variable compositions.

5 The object of this invention is achieved by a process for acid-catalyzed hydrolysis of a carboxylic ester to the corresponding carboxylic acid and the corresponding alcohol in the presence of water by passing an inlet stream comprising the carboxylic ester mixed with water into a first prereactor having a
10 hydrolysis catalyst, which hydrolyzes the carboxylic ester at least partly to the hydrolysis products, removing the reaction mixture from this first prereactor and passing it at least partly into a reactive distillation column comprising a hydrolysis catalyst, which converts the carboxylic ester stream
15 comprising water further to carboxylic acid and alcohol and simultaneously at least partly separates it into the components, the mixtures comprising the less volatile compounds and the low-boiling carboxylic esters being removed at least partly as a distillate, for example as a top fraction, and the
20 less volatile compounds collecting at least partly as a bottom fraction which is passed into a further distillation column, which comprises feeding the aqueous carboxylic acid from the bottom fraction or from the lower rectification zone on the distillation column, mixed with further carboxylic ester, to a
25 second prereactor comprising a hydrolysis catalyst, removing the reaction mixture from the second prereactor and passing it at least partly into the reactive distillation column.

In this context, the distillate of the reactive distillation
30 column is defined as every fraction withdrawn from the distillation column above the reaction zone, including the entire condensation system of the reactive distillation column, for example a sidestream or a fraction withdrawn by partial condensation, a substream or the entire top fraction or else
35 fractions thereof.

Advantageously, at least a portion of the bottom fraction of the reactive distillation column is fed to at least one further

distillation column and is separated at least partly into the
components. Preference is given to using one or more downstream
separating stages when the resulting reaction mixture is to be
separated into the individual components. The bottom fraction
5   or a fraction from the lower rectification zone, preferably a
fraction from the lower half of the rectification zone of this
distillation column, comprising the resulting carboxylic acid
and water, is fed at least partly to the second prereactor, in
which case it can be mixed beforehand with the new carboxylic
10   ester feed or with the distillate of the reactive distillation
column which occurs directly or has been concentrated in
carboxylic ester by means of further separating steps and
comprises carboxylic ester which is yet to be converted and was
originally fed to the inlet of the first prereactor.
15

When mixing the aqueous carboxylic acid from the bottom
fraction of the distillation column or a fraction from the
lower rectification zone, it is advantageous that this stream
already has an elevated temperature of from 50 to 150°C, and
20   when mixing with the stream comprising carboxylic ester for
entry into the second prereactor, the resulting mixture heats
to temperatures of from 50 to 100°C. It is therefore not
necessary to again feed energy to the process in the form of
heat to heat the feed of the second prereactor.
25

The carboxylic ester stream for the overall process, which is
fed to one or both prereactors, is advantageously mixed with at
least an equimolar amount of water. The molar ratio between
carboxylic ester and water is appropriately between 1:1 and
30   1:15, preferably between 1:2 and 1:10 and more preferably
between 1:4 and 1:8.

The hydrolysis reaction can also be carried out at room
temperature. Preference is given to heating the mixture of
35   carboxylic ester and water to a temperature between 30 and
120°C, more preferably to from 50 to 100°C, since the
hydrolysis equilibrium is shifted at elevated temperatures
advantageously to the side of the carboxylic acid and alcohol

products, and the reaction rate is increased. The selection of the temperature is characterized substantially by the thermal stability of the ion exchanger.

5   The reactive distillation column is particularly advantageously operated in such a way that the carboxylic acid and at least a portion of the water and of the alcohol remain in the bottom fraction of the reactive distillation column. In this case, the reaction mixture from the first prereactor is introduced into
10   the reactive distillation column, preferably into the reactive distillation column at a point in the upper third of the catalyst zone or above the catalyst zone and below the upper rectification zone. In the case of the hydrolysis of relatively high-boiling carboxylic acids which form a low-boiling, water-
15   rich, usually ternary, azeotrope, for example isobutyl acetate, it is advantageous to feed it in at a point below the reaction zone and above the lower rectification zone or in the upper third of the lower rectification zone. The reaction mixture from the second prereactor is advantageously fed in below the
20   reaction zone and above the lower rectification zone, or in the case of the hydrolysis of relatively high-boiling carboxylic acids which form a water-rich, usually ternary azeotrope, advantageously into the upper third of the lower rectification zone. The bottom fraction which occurs and comprises, for
25   example, alcohol, water and carboxylic acid is fed to a further distillation column in which the mixture is separated further.

The distillate of the reactive distillation column, directly or after passing through further separation or distillation
30   stages, can be fed partly to the first prereactor, to the second prereactor or both prereactors, in order to further convert any carboxylic ester still present in the distillate. Such recycling of the distillate of the reactive distillation column allows the capacity of the plant to be substantially
35   increased.

As a consequence of the typically rising content of low-boiling impurities which are at least partly discharged at the top of

the reactive distillation column, and of the water content
rising toward the catalyst zone in the case of a feed, which is
preferably disposed above the catalyst zone, into the reactive
distillation column, it is advantageous to withdraw the
5   distillate from the upper rectification zone which is
preferably disposed above the catalyst zone, preferably in its
lower third.

The process according to the invention is preferably operated
10 continuously, i.e. carboxylic ester and water are passed
continuously into the first prereactor and the resulting
reaction mixture is removed continuously from the first
prereactor and passed into the reactive distillation column in
which unconverted carboxylic ester is for the most part
15 converted to its hydrolysis products. In the continuous
process, the hydrolysis products are removed continuously in
the distillate, in the top fraction and in the bottom fraction,
and, preferably, the distillate, directly or after passing
through further separation or distillation stages to
20 concentrate the carboxylic ester, is continuously fed back to
the first prereactor, to the second prereactor, or to both
prereactors, the bottom fraction is likewise fed continuously
to a distillation column and the aqueous carboxylic acid in the
bottom fraction or a fraction from the lower rectification
25 zone, preferably from the lower half of the lower rectification
zone, of this distillation column is fed at least partly, mixed
with carboxylic ester, to the second prereactor. The volume
stream fed per unit volume of hydrolysis catalyst in both
prereactors is advantageously between $0.1 - 15 \ h^{-1}$, preferably
30 $0.5 - 8 \ h^{-1}$ and more preferably between $1 - 4 \ h^{-1}$.

The present invention also provides an apparatus for acid-
catalyzed hydrolysis of a carboxylic ester to the corresponding
carboxylic acid and the corresponding alcohol in the presence
35 of water, comprising
a)   a first prereactor **1** comprising a hydrolysis catalyst and
having at least one inlet line **2** for feeding in a fluid
stream comprising the carboxylic ester, line **2'**, and water,

line **2''**, and also at least one outlet **4** for removing the reaction mixture,

b) at least one heating apparatus for heating the inlet stream, line **2**, of the first prereactor **1**, or both,

c) a second prereactor **19** comprising a hydrolysis catalyst and having at least one inlet for a fluid stream comprising at least partly the aqueous carboxylic acid from the bottom fraction or a fraction of the lower rectification zone **14** of the distillation column **13**, line **18**, also mixed with a carboxylic ester stream, line **20**, and at least one outlet, line **25**,

d) a reactive distillation column **7** comprising a catalyst zone **8** having a hydrolysis catalyst and having an inlet **6** connected to the first prereactor **1**, an inlet connected to the second prereactor, line **25**, the catalyst zone **8** being disposed between a lower rectification zone **9** and an upper rectification zone **10**,

e) line **22** attached at the distillation head or at the condensation system of the reactive distillation column for removing the top fraction or as a purge,

f) line **21** connecting to the line **22** conducting the top fraction of the reactive distillation column **7** or connecting to the upper distillation part **10** including the entire condensation system of the reactive distillation column **7**, for removing distillate,

g) line **11** attached at the distillation bottom of the reactive distillation column **7**, for removing the bottom fraction,

h) a distillation column **13**, the line **11** forming the inlet for removing the bottom fraction of the reactive distillation column **7**, at whose distillation bottom, line **26**, aqueous carboxylic acid is removed,

i) line **18** conducting a fraction of aqueous carboxylic acid withdrawn from the lower rectification zone **14** of the distillation column **13** or a portion of line **26**, this forming the inlet to the second prereactor **19**, mixed with the carboxylic ester, line **20**.

In a preferred embodiment, the first or second prereactor independently has two reaction chambers. In addition, means may be provided to be able to pass the feed stream in each case through one of the reaction chambers, so that the other

5 reaction chamber in each case can be charged with fresh catalyst. This has the advantage that the equipment can be operated continuously over a long period. In a further preferred embodiment, the first or second prereactor independently has a bypass, in order to likewise ensure the

10 exchange of the structured catalyst packing without interrupting the continuous operation of the apparatus.

The reactive distillation column **7** preferably has a catalyst zone **8** and also a lower (**9**) and an upper rectification zone **10**,

15 and the catalyst zone **8** is disposed between the lower and the upper rectification zone (**9,10**). The rectification zones may have separating trays, Raschig rings, structured mass transfer packings or the like.

20 The first prereactor **1**, the second prereactor **19** or the reactive distillation column **7** are advantageously each independently configured as a tube. In this tube, a hydrolysis catalyst can be charged in a random manner or arranged in a structured catalyst packing. The hydrolysis catalysts are

25 appropriately acidic solid catalysts, preferably having a particle size of between about 0.3 and 3 mm, with preference between 0.6 and 1.2 mm. While the hydrolysis catalysts in the prereactors (**1, 19**) are preferably in the form of spheres, rings, extrudates, etc., as a random packing, the hydrolysis

30 catalyst of the reactive distillation column **7** is advantageously installed as a structured catalyst packing. Suitable structured catalyst packings are described, for example, in the patent specifications US 5,417,939, US 5,470,542 and US 5,536,699, whose disclosure contents on this

35 subject is incorporated herein by reference. In this context, a structured catalyst packing is a structure having retaining features (e.g. pockets) for solid catalyst material and having flow channels which are provided in the structure. It is also

conceivable to use such structured catalyst packings both in the prereactors (**1, 19**) and in the reactive distillation column **7**. The prereactors (**1, 19**) may also, for example, be configured in the form of stirrers having installed or fluidized catalyst.

5 The reactive distillation column **7** selected may be a tray column, and the ion exchanger as the catalyst may be disposed on the trays themselves and in the downcomers.

In a further preferred embodiment, the inlet line **2** to the
10 first prereactor is heated by mixing the carboxylic ester stream, line **2'**, with hot water, line **2''**, for example heating vapor condensate, in order to thus set the desired reaction temperature. In this preferred embodiment, a further heating apparatus of the feed of the first prereactor and also of the
15 prereactor itself can be dispensed with.

Figure 1 shows a schematic illustration of a preferred embodiment of the inventive apparatus. The first prereactor **1** has an inlet line **2** for introducing a fluid stream into the
20 reactor chamber **3** containing the hydrolysis catalyst, preferably an acidic solid catalyst, and an outlet **4**, for removing the reaction mixture. The connecting line **5** connects the outlet **4** of the first prereactor to an inlet **6** to the reactive distillation column **7**. The first prereactor **1** is
25 preferably tubular, and the inlet line **2** is supplied from the feed of the carboxylic ester mixture to be hydrolyzed, line **2'**, and the feed of the water, line **2''**. The first prereactor **1** has a hydrolysis catalyst which is disposed in the reactor chamber **3**.

30
The reactive distillation column **7** has a catalyst zone **8** and a lower rectification zone **9** and also an upper rectification zone **10** which are arranged below and above the catalyst zone **8** respectively. The catalyst zone **8** contains a hydrolysis
35 catalyst, preferably an acidic solid catalyst, more preferably in a structured catalyst packing. The rectification zones are formed, for example, by Raschig rings, column trays, structured (mass transfer) packings or the like in a known manner. At the

bottom of the column of the lower rectification zone **9**, a line
11 is provided for removing the bottom fraction and, at the top
of the column of the upper rectification zone **10**, a line **22** is
provided for removing the top fraction of the reactive
5   distillation column **7**. The feed of the products of the first
prereactor **1**, line **5**, is preferably above the reaction zone **8**
and below the upper rectification zone **10** or in the upper third
of the reaction zone **8**. In the case of higher-boiling
carboxylic esters which form a low-boiling, water-rich, usually
10   ternary, azeotrope, it is advantageous to feed in below the
reaction zone **8** and above the upper rectification zone **9** or in
the upper third of the lower rectification zone **9**.

The line **11** is connected to a distillation column **13**. The
15   distillation column **13** preferably has a lower rectification
zone **14** and an upper rectification zone **15**. The line **11** is
preferably attached between the rectification zones **14** and **15**
of the distillation column **13**. The reaction product withdrawn
from the distillation column **13** is aqueous carboxylic acid as
20   the bottom fraction whis is removed via line **26**. A portion of
the aqueous carboxylic acid is withdrawn either from line **26**,
the bottom of the distillation column **13**, or from the lower
rectification zone **14**, preferably the lower half of the lower
rectification zone **14**, and at least partly·fed to the second
25   prereactor **19** via line **18**. Upstream of entry into the second
prereactor **19** having the reaction chamber **27** filled with
hydrolysis catalyst, preferably an acidic solid catalyst,
further carboxylic ester is fed to line **18** via line **20**.

30   The second prereactor has a catalyst zone **27** which preferably
contains an acidic solid catalyst. The second prereactor is
preferably flowed through from bottom to top. The outlet of the
second prereactor is connected to the reactive distillation
column **7** by means of the line **25**. The line **25** is preferably
35   conducted into the reactive distillation column **7** below the
catalyst zone **8** and above the lower rectification zone **9**. In
the case of the hydrolysis of relatively high-boiling
carboxylic esters having a high water content in the ternary

azeotrope, the feed from the second prereactor into the hydrolysis column can optionally be optimized by passing it into the upper third of the lower rectification column **9**.

5 The line **22** for removing the top fraction of the reactive distillation column **7** comprising unconverted carboxylic ester can be connected via line **21** to line **2**, line **2'** or line **2''** of the carboxylic ester mixture to be hydrolyzed. A portion of the top fraction of the reactive distillation column **7** is withdrawn
10 via line **22**, in order to withdraw low boilers and inerts from the apparatus (purge). This also avoids an accumulation which is hazardous to safety of low boilers, for example acetaldehyde.

15 In a preferred embodiment, the carboxylic ester which has not been converted in the reactive distillation column **7** is withdrawn by means of line **21** not from line **22**, but from the upper rectification zone of the reactive distillation column **7**.

20 The alcohol formed or released is preferably withdrawn at the upper rectification zone **15** of the distillation column **13** by means of lines **23** or **24**. The advantage of withdrawing the alcohol via line **24** is that the distillate enriched with carboxylic ester of line **23** from the distillation column **13** can
25 be recycled into the reactive distillation column **7** and fed in there preferably below the catalyst zone **8** and above the lower rectification zone **9** or in the upper third of the lower rectification zone **9**. Recycling into the process by connecting. line **23** to the first prereactor **1** and into the second
30 prereactor **19** is likewise possible.

In order to prevent partial evaporation of the feed to a second prereactor **19**, it is advantageous to allow the mixing of the aqueous carboxylic acid and the carboxylic ester-containing
35 feed, and also the reaction in the second prereactor **19**, to take place under elevated pressure. The elevated pressure required depends on the mixing ratio and the system

composition, and preference is given to pressures in the range
from 1 to 6 bar.

A second preferred embodiment of the inventive apparatus is
5   reproduced in figure 2. The inventive apparatus according to
drawing 2 differs from the inventive apparatus in figure 1 in
that the line **21** is not connected to the feed of the carboxylic
ester mixture to be hydrolyzed **2'**, to the water feed **2''** or to
the mixture **2**, but rather to the line **18** which conducts the
10   aqueous carboxylic acid from the bottom fraction of the
distillation column **13** into the second prereactor **19**. The feed
20 is accordingly dispensed with, and the line **21** may be
connected to the line **22** or, in a further preferred embodiment,
may be withdrawn from the upper rectification zone **10**.
15

A further preferred embodiment of the inventive apparatus is
reproduced in figure 3. This inventive apparatus differs from
the inventive apparatus in figure 2 in that the line **23** for at
least partial removal of the distillate from the distillation
20   column **13** into the reactive distillation column **7** is connected
to the latter. The line **23** is conducted into the reactive
distillation column **7** preferably below the catalyst zone **8** and
above the lower rectification zone **9** or in the upper third of
the lower rectification zone **9**.   ,
25

Further preferred embodiments for the hydrolysis of relatively
high-boiling carboxylic esters having an increased water
content in the low-boiling, usually ternary azeotrope are
reproduced in figures 4 and 5. These inventive apparatus differ
30   from the inventive apparatus in figures 2 and 1 in that the
product of the first prereactor **1** is fed into the reactive
distillation column **7** preferably below the reaction part **8** and
above the rectification zone **9** or in the upper third of the
lower rectification zone **9**. The product of the second
35   prereactor **19** is fed in below the reaction zone **8**, preferably
in the upper third of the lower rectification zone **9**.

The process according to the invention can be used to hydrolyze preferably the carboxylic esters methyl and ethyl formate, methyl, ethyl, propyl, isobutyl and tert-butyl acetate, methyl and ethyl propionate, and also methyl, ethyl and propyl
5   butyrate, in particular methyl acetate.

An inventive process and also an inventive apparatus for hydrolyzing a carboxylic ester is now to be described by way of example using the acid-catalyzed hydrolysis of methyl acetate.
10   A fluid stream comprising the azeotrope of methyl acetate and methanol, corresponding to a molar ratio of 1.94:1, from polyvinyl alcohol production, is mixed with an at least equimolar amount of water, preferably a 4- to 7-fold molar excess of water, based on methyl acetate. The water used is hot
15   water which heats the mixture to a temperature between 50 and 80°C. The mixture is passed into the first prereactor 1 which is preferably arranged vertically.

The first prereactor 1 is packed with a cationic ion exchanger
20   as an acidic solid catalyst. The catalyst preferably has a particle size between about 0.35 and 3 mm. Such a catalyst material is obtainable, for example, under the name Amberlyst 15® from Rohm & Haas. Alternative catalysts are, for example, zeolites, alumina, silica, etc.
25

The mixture of methyl acetate and water flows through the first prereactor 1 and is contacted with the catalyst material. This results in partial hydrolysis of the methyl acetate. The conversion of the methyl acetate in the first prereactor 1 is
30   between 20 and 100%, preferably between 60 and 100%, of the equilibrium conversion. The resulting reaction mixture is introduced via line 5, preferably above the catalyst zone 8 and below the rectification zone 10 of the reactive distillation column 7.
35

The reactive distillation column 7 is preferably operated in such a way that the two hydrolysis products, methanol and acetic acid, are removed from the bottom fraction together with

the unconverted water. The remaining, volatile methyl acetate
is removed from the reaction products in the lower
rectification zone **9** and concentrated distillatively in the
catalyst zone **8** for hydrolysis. The reaction products formed,
5   methanol and acetic acid, are permanently discharged
distillatively from the catalyst zone **8** into the lower
rectification zone **9** or into the bottom fraction, line **11**.

The mixture of acetic acid, water and methanol which is
10   obtained in the bottom fraction of the reactive distillation
column **7** is further separated in the downstream distillation
column **13**, in which methanol is removed at the top of the
column or at the upper distillation zone **15** and the mixture of
acetic acid and water is obtained in the bottom fraction of the
15   distillation column **13**. This aqueous acetic acid is removed via
line **26** and at least partly fed via line **18** into the second
prereactor **19**. Alternatively, the recycling amount of aqueous
carboxylic acid can be withdrawn by means of a sidestream
takeoff of the lower rectification zone **14**, preferably from its
20   lower half.

Before entry into the second prereactor **19** via line **20**, further
methyl acetate is fed to line **18**. In a further preferred
embodiment, a methyl acetate stream is fed in via line **20** and
25   preferably contains from 50 to 100%, more preferably from 90 to
100%, methyl acetate. This methyl acetate stream is, for
example, supplied from methyl acetate which has already been
further purified and is obtained, for example, from polyvinyl
alcohol production. The aqueous acetic acid from the bottom
30   fraction of the distillation column **13** has a temperature higher
than 30°C, preferably from 50 to 110°C, more preferably from
100 to 105°C. The mixing with the methyl acetate heats the
inlet stream of the second prereactor **19** already to
temperatures of from 25 to 100°C, preferably to from 50 to
35   90°C, more preferably to from 70 to 90°C. The mixing of the
feeds and the reaction in the second reactor proceeds as a
consequence of the high vapor pressure of methyl acetate,
preferably under elevated pressure.

The second prereactor **19** preferably has an acidic solid
catalyst. The second prereactor **19** is preferably flowed through
from bottom to top and is operated at a preferred temperature
of from 50 to 120°C, more preferably from 70 to 90°C. The
conversion of the methyl acetate is between 20 and 100%,
preferably between 60 and 100%, of the equilibrium conversion.
The outlet of the second prereactor **19** is connected to the
reactive distillation column **7** by means of line **25**. The line **25**
is conducted into the reactive distillation column **7** preferably
below the catalyst zone **8** and above the lower rectification
zone **9** or in the upper third of the lower rectification zone **9**.

In a further preferred inventive embodiment, the line **21**
conducting distillate from the reactive distillation column **7**,
optionally containing unconverted methyl acetate, is fed to
line **18**. The line **20** is accordingly dispensed with. This
embodiment has the advantage that unconverted methyl acetate is
fed to the hydrolysis in the second prereactor **19** and
optionally to the reactive distillation column **7**.

The temperature in the first prereactor **1**, second prereactor **19**
and in the reactive distillation column **7** is determined as a
function of pressure, and a certain elevated pressure allows a
higher temperature and therefore a higher reaction rate and a
more favorable equilibrium position. Preference is given to
operating the apparatus or parts of the apparatus at elevated
pressures of from 1 to 6 bar, more preferably from 1.5 to 3
bar.

Deviating from the design of a plant in accordance with the
prior art, where process feed having a molar ratio of methyl
acetate to methanol of 1.94:1 corresponding to the azeotrope is
introduced into the process, this, as a consequence of the
shifting of the equilibrium reaction at the expense of the
products, reduces the maximum available capacity of a plant
according to the prior art. The increased recycling of methyl
acetate-rich distillate from the reactive distillation column **7**

to the first prereactor **1** and the very substantially fixed geometry of the catalyst zone **8** of the reactive distillation column **7** restricts the extent of a capacity increase using the existing structure.

5

An azeotrope of methyl acetate and methanol is not preferred as a feed for the second prereactor **19**, since the alcohol content thus fed in shifts the equilibrium reaction of the acidic hydrolysis unfavourably for the products. As already mentioned,

10 the molar ratio of methyl acetate to methanol in the azeotrope is 1.94:1. In the top fraction having a high methyl acetate content and in the distillate of the reactive distillation column **7**, the ratio is about 4:1 or higher, which is considerably more favorable for the conversion. It is therefore

15 particularly advantageous to introduce the distillate of the reactive distillation column **7** into the second prereactor **19**, instead of feeding it to the feed of the first prereactor **1**. In addition, a decrease in the distillate from the upper rectification zone **10** of the reactive distillation column **7**

20 favors the conversion as a result of the lower content of low boilers to be discharged and the water content rising toward the catalyst zone **8**. A ratio of only 1:1 is suitable for converting about 33% of the methyl acetate fed which is diluted by approx. 35% by weight of acetic acid. This means that the

25 amount of distillate fed, line **21**, to the reactive distillation column **7** can be used to optimize the methyl acetate conversion. This equally applies to the recycled aqueous carboxylic acid stream, line **18**. An increased inlet stream of azeotrope of metyl acetate and methanol to the first prereactor **1** replaces

30 the amount of distillate which is no longer present, line **21**, of the reactive distillation column **7** and thus allows the capacity increase.

The high exit temperature of the aqueous acetic acid at the
35 stripping section of the distillation column **13** of preferably from 100 to 105°C enables a mixing temperature with the methyl acetate in the order of magnitude from 70 to 90°C, which favors the hydrolysis of the methyl acetate fed in the second

prereactor **19**. Particular preference is given to process operation under slightly elevated pressure of from 1.5 to 3 bar. The operation under elevated pressure can be taken into account simply by suitable pipeline control.

The recycling of dilute acid to a second prereactor **19** and the feeding into the reactive distillation **7** leads to a distinctly increased fluid dynamic loading of the stripping sections (**9, 10**) of the reactive distillation column **7** and the optional downstream distillation column **13**.

The capacity of a prior art plant can be estimated at an additional 80 to 100% by introducing a second prereactor **19** and recycling the aqueous carboxylic acid, and the specific heating vapor requirements of the plant only increases slightly.

The incorporation of the second prereactor 19 is simple from the point of view of installation and process technology. The embodiment which is preferred in accordance with the invention likewise allows more highly concentrated aqueous acetic acid to be produced by not increasing the water feed to the first prereactor **1** proportionally to the amount of methyl acetate.

In the experimental examples which follow, the catalyst used is a commercial cationic solid catalyst. In the reactive distillation column **7** the catalyst was installed in a structured catalyst packing.

Example 1 (comparative example):

A combination of the prereactor **1** with reactive distillation column **7** was used. There was no recycling of distillate from the reactive distillation column **7** to the prereactor **1** by means of line **21**. The methyl acetate stream to be hydrolyzed had approximately the azeotropic composition of 81% by weight of methyl acetate and 19% by weight of methanol. The bottom fraction of the reactive distillation column **7** comprises methanol, acetic acid, water and traces of methyl acetate. This

mixture was separated in the distillation column **13** into a
methanol stream comprising traces of methyl acetate and into an
acetic acid/water mixture.

5 Reactive distillation column **7**:

Diameter:	1100 mm
Upper rectification zone **10**:	5 theoretical plates
Catalyst zone **8**:	3 theoretical plates
Lower rectification zone **9**:	8 theoretical plates

10

Feed streams:

Azeotrope, line **2'**:	700 kg/h
Water, line **2''**:	900 kg/h

15 Product streams:

Top fraction (purge),
Line **22**, of the reactive
distillation column **7**:   26 kg/h
Bottom fraction, line **11**,
20 of the reactive
distillation column **7**:   1574 kg/h

Experimental conditions:
Top pressure of reactive
25 distillation column **7**:   26 mbar gauge
Feed point of reactive
distillation column **7**:   above the catalyst zone **8**
Heating output of reactive
distillation column **7**:   700 kW
30 Heating output of
distillation column **13**:   490 kW
Entrance temperature
to prereactor **1**:   58°C

35 Result:
Methyl acetate conversion
in the prereactor **1**:   41.8%
Overall methyl acetate

conversion: 98.9%

                                   neglecting the purge, line **22**)

Composition of bottom fraction, line **11**, of the reactive

distillation column **7**:

Methyl acetate: 0.4% by weight

Methanol: 22.7% by weight

Water: 49.6% by weight

Acetic acid: 27.3% by weight

Composition of top fraction, line **23**, of the distillation

column **13**:

Methyl acetate: 2.0% by weight

Methanol: 98.0% by weight

Composition of bottom fraction, line **26**, of the distillation

column **13**:

Water: 64.3% by weight

Acetic acid: 35.7% by weight

Example 2 (comparative example - process with recycling):

A combination of the prereactor **1** with reactive distillation
column **7** was used. There was recycling of distillate from the
reactive distillation column **7** to the prereactor **1** by means of
line **21**. The methyl acetate stream to be hydrolyzed had
approximately the azeotropic composition of 81% by weight of
methyl acetate and 19% by weight of methanol. The bottom
fraction of the reactive distillation column **7** comprises
methanol, acetic acid, water and traces of methyl acetate. This
mixture was separated in the distillation column **13** into a
methanol stream comprising traces of methyl acetate and into an
acetic acid/water mixture.

Reactive distillation column **7**:

Diameter: 1100 mm

Upper rectification zone **10**:   5 theoretical plates

Catalyst zone **8**:   3 theoretical plates
Lower rectification zone **9**:   8 theoretical plates

Feed streams:

5   Azeotrope, line **2′**:   685 kg/h
Water, line **2′′**:   930 kg/h

Product streams:
Top fraction (purge),
10 Line **22**, of the reactive
distillation column **7**:   15 kg/h
Bottom fraction, line **11**,
of the reactive
distillation column **7**:   1600 kg/h
15

Experimental conditions:
Top pressure of reactive
distillation column **7**:   29 mbar gauge
Feed point of reactive
20 distillation column **7**:   above the catalyst zone **8**
Distillate recycling,
line **21**, to preactor **1**:   1985 kg/h
Heating output of reactive
distillation column **7**:   490 kW
25 Heating output of
distillation column **13**:   490 kW
Entrance temperature
to prereactor **1**:   58°C

30 Result:
Methyl acetate
conversion: 99.1%
                                      neglecting the purge, line **22**)

35 Composition of bottom fraction, line **11**, of the reactive
distillation column **7**:
Methyl acetate: 0.3% by weight

Methanol:	22.7% by weight
Water:	50.0% by weight
Acetic acid:	27.4% by weight

Composition of top fraction, line **23**, of the distillation column **13**:

Methyl acetate:	1.5% by weight
Methanol:	98.5% by weight

Composition of bottom fraction, line **26**, of the distillation column **13**:

Water:	64.6% by weight
Acetic acid:	35.4% by weight

Example 3:

A combination of two prereactors **1** and **19** having a reactive distillation column **7** according to figure 2 was used. The methyl acetate stream to be hydrolyzed had approximately the azeotropic composition of 81% by weight of methyl acetate and 19% by weight of methanol. The bottom fraction of the reactive distillation column **7** comprises methanol, acetic acid, water and traces of methyl acetate. This mixture was separated in the distillation column **13** into a methanol stream comprising traces of methyl acetate and into an acetic acid/water mixture.

Reactive distillation column **7**:

Diameter:	1100 mm
Upper rectification zone **10**:	5 theoretical plates
Catalyst zone **8**:	3 theoretical plates
Lower rectification zone **9**:	8 theoretical plates

Feed streams:

Azeotrope, stream **2'**:	1600 kg/h
Water, stream **2''**:	2200 kg/h

Product streams:
Top fraction (purge),
Line **22**, of the reactive
distillation column **7**:   30 kg/h

5 Bottom stream, line **11**,
of the reactive
distillation column **7**:   6170 kg/h
Distillate recycling,
line **21**,

10 to second prereactor **19**:   3000 kg/h

Dilute acid recycling,
line **18**, to second
prereactor **19**:   2400 kg/h

15

Top fraction, line **23**, of the
distillation column **13**:   870 kg/h
Bottom fraction, line **26**,
of the distillation column **13**: 2900 kg/h

20

Experimental conditions:
Top pressure of the reactive
distillation column **7**:   30 mbar gauge
Inlet **6** into reactive

25 distillation column **7**:   above the catalyst zone **8**
Inlet of the line **25**
into reactive distillation
column **7**:   below the catalyst zone **8**
Heating output of reactive

30 distillation column **7**:   1200 kW
Heating output of
distillation column **13**:   1350 kW
Entrance temperature to
prereactor **1**:   62°C

35 Entrance temperature to
prereactor **19**:   88°C

Result:

Methyl acetate conversion:	98.8%
	neglecting the purge, line **22**)

Composition of bottom fraction, line **11**, of the reactive distillation column **7**:

Methyl acetate:	0.3% by weight
Methanol:	14.0% by weight
Water:	55.7% by weight
Acetic acid:	30.0% by weight

Composition of top fraction, line **23**, of the distillation column **13**:

Methyl acetate:	1.8% by weight
Methanol:	98.2% by weight

Composition of bottom fraction, line **11**, of the distillation column **13**:

Water:	65.0% by weight
Acetic acid:	35.0% by weight

Example 4:

A combination of two prereactors **1** and **19** having a reactive distillation column **7** according to figure 3 was used. The feed of methyl acetate was increased and the water excess reduced. The methyl acetate stream to be hydrolyzed had approximately the azeotropic composition of 81% by weight of methyl acetate and 19% by weight of methanol. The bottom fraction of the reactive distillation column **7** comprises methanol, acetic acid, water and traces of methyl acetate. This mixture was separated in the distillation column **13** into a methanol stream comprising traces of methyl acetate and into an acetic acid/water mixture.

Reactive distillation column **7**:

Diameter:	1100 mm
Upper rectification zone **10**:	5 theoretical plates
Catalyst zone **8**:	3 theoretical plates

Lower rectification zone **9**:   8 theoretical plates

Feed streams:
Azeotrope, line **2'**:   1700 kg/h
Water, line **2''**:   1700 kg/h

Product streams:
Top fraction (purge),
Line **22**, of the reactive
distillation column **7**:   35 kg/h
Bottom fraction, line **11**,
of the reactive
distillation column **7**:   6865 kg/h
Distillate recycling,
line **21**,
to second prereactor **19**:   3500 kg/h
Dilute acid recycling,
Line **18**, to second
prereactor **19**:   3500 kg/h
Distillate, line **23**, of the
distillation column **13**:   930 kg/h
Bottom fraction, line **26**,
of the distillation column **13**:   2435 kg/h

Experimental conditions:
Top pressure of the reactive
distillation column **7**:   37 mbar
Inlet **6** into reactive
distillation column **7**:   above the catalyst zone **8**
                                       (neglecting the purge, line **22**)
Inlet of the line **25**
into reactive distillation
column **7**:   below the catalyst zone **8**
Heating output of reactive
distillation column **7**:   1300 kW
Heating output of
distillation column **13**:   1300 kW
Entrance tempreature to

prereactor **1**:   65°C

Entrance temperature to

prereactor **19**:   77°C

5   <u>Result:</u>

Methyl acetate conversion: 98.2%

<u>Composition of bottom fraction, line **11**, of the reactive
distillation column **7**:</u>

10   Methyl acetate: 0.4% by weight

Methanol: 13.3% by weight

Water: 48.4% by weight

Acetic acid: 37.9% by weight

15   <u>Composition of top fraction, line **23**, of the distillation
column **13**:</u>

Methyl acetate: 2.7% by weight

Methanol: 97.3% by weight

20   <u>Composition of bottom fraction, line **26**, of the distillation
column **13**:</u>

Water: 56.1% by weight

Acetic acid: 43.9% by weight

25   **Example 5:**

As a further inventive example, the hydrolysis of isobutyl
acetate to isobutanol and acetic acid is considered by means of
process simulation. Isobutyl acetate was selected because its
30   normal boiling point within the group of isobutyl acetate,
isobutanol, acetic acid and water is the highest. The boiling
points of the two reaction products, isobutanol and acetic
acid, are above that of the reaction partner water.

35   <u>Normal boiling points:</u>

Isobutyl acetate (iBuAc):   117.2°C

Water (H_2O):   100.0°C

Isobutanol (iBuOH):   107.9°C

Acetic acid (AA):   117.9°C

Binary azeotropes:

5   77.7% by weight of isobutyl acetate, 22.3% by weight of water;
normal boiling point: 88.4°C

44.9% by weight of isobutyl acetate, 55.1% by weight of
isobutanol;
normal boiling point: 105.1°C

10   66.8% by weight of isobutanol, 33.2% by weight of water;
normal boiling point: 89.9°C

Ternary azeotrope

46.5% by weight of isobutyl acetate, 30.4% by weight of water,

15   23.1% by weight of isobutanol; normal boiling point: 86.8°C

52.3% by weight of isobutyl acetate, 21.3% by weight of water,
26.4% by weight of isobutanol, normal boiling point: 86.6°C

The process was carried out on the basis of equilibrium

20   calculations with respect to the mass transfer and the chemical
conversion. The dimerization of the carboxylic acid was taken
into account by the approach of Hayden O'Connel. For the
description of the chemical equilibrium, the equilibrium
constant according to formula (1)

25

$$K_x = (x(iBuOH)*x(AA))/(x(iBuAc)*x(H_2O)) = 0.05 \text{ mol}^2/\text{mol}^2 \qquad (1)$$

was used.

30   The process configuration selected is illustrated in figure 5.
It is based on figure 1, except that the feed points to the
reactive distillation column **7** were adapted to the boiling
conditions of the system.

35   Reactive distillation column **7**:

Upper rectification zone **10**:   stage 1 to 4;
                                      4 theoretical plates

Catalyst zone **8**:   stage 5 to 7;

lower rectification zone **9**:   3 theoretical plates
stage 8 to 23;
16 theoretical plates

Reflux ratio: 1.12

Feed to the first
prereactor **1**:   above stage 8; below catalyst
zone **8**

Feed to second
prereactor **19**:   above stage 11; in the upper
third of the lower rectification
zone **9**

First prereactor **1**:   Temperature: 100°C
Pressure: 1 bar gauge
Chemical equilibrium

Second prereactor **19**:   Temperature: 100 °C
Pressure: 1 bar gauge
Chemical equilibrium

Distillation column **13**:   28 separating stages
Reflux ratio: 2.5

Connection: Line **21** branches off from line
22
Line **18** branches off from line
26

<u>Feed and product streams:</u>

Line	2′	2′′	20	5	11	18	21	22	23	25	26
Flow rate (kg/h)	1000	1980	350	8914	8264	5000	5934	66	1400	5350	1864
H_2O (% by wt.)		100		37.0	60.6	64.8	24.7	24.7	39.9	60.4	64.8
iBuAc (% by wt.)	97.0		97.0	33.1	0.01		48.7	48.7	0.09	5.1	
AA (% by wt.)				5.3	29.2	35.2				33.5	35.2

iBuOH (% by wt.)	3.0		3.0	24.6	10.1		26.6	26.6	60.1	1.0	

The comparison of the simulation of the hydrolysis of isobutyl acetate by means of a connection of the prereactor **1** to the reactive distillation column **7** and the recycling of equal amounts of distillate by means of line **21** at the same heating output and the same water excess, line **2''**, shows that only the proceed feed **2'** of 1000 kg/h can be converted. The inventive incorporation of the second prereactor **19** thus allows the process flow rate of 1350 kg/h to be hydrolyzed. This corresponds to a capacity increase of 35%.